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# Element Associations in Soils of the San Joaquin Valley of California<sup>1</sup>

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## ABSTRACT

Total chemical analyses of soils on the alluvial fans of Panoche and Cantua Creeks in western Fresno County, California, were studied to identify associations among elements in the soils. Some elements, particularly Se, have been identified as pollutants in agricultural drainage water from this area. Samples of the C-horizon from 168 to 183 cm were analyzed for total concentrations of 43 elements. An R-mode factor analysis of data for 26 elements suggested five element associations in the soils. Factor 1, predominantly Al, Ti, gallium (Ga), yttrium (Y), Cerium (Ce), scandium (Sc), Fe, and Li, is interpreted as a felsic-sediment factor. Factor 2, predominantly Ni, Mg, Cr, Co, Mn, and Fe, is related to serpentine. Factor 3, Se and S, reflects the similar chemical behavior of these two elements; Na is negatively related to this factor. Selenium is probably hosted in sedimentary rocks that border the valley. Factor 4, Ca, Sr, C, and S, is an alkaline-earth factor related to carbonate and sulfate precipitation. Factor 5, C and Hg, reflects common alluvial sedimentation.

Subsurface agricultural drainage collected from a part of the San Luis irrigation district (San Luis Drain Service Area, Central Valley project, San Joaquin Valley) in western Fresno County, California (Fig. 9-1), contains elevated levels of several trace elements, of which Cr, Hg, and Se exceed water quality criteria for freshwater aquatic life (Deverel et al., 1984). The drainage is transported through the San Luis Drain to Kesterson National Wildlife Refuge in Merced County (San Joaquin Valley Interagency Drainage Program, 1979), where a high incidence of mortality and birth defects among waterfowl has been observed (U.S. Bureau of Reclamation, 1984). This toxicity is believed to result from Se because high concentrations of this ele-

<sup>1</sup>Contribution from the U.S. Geological Survey, Denver, CO.

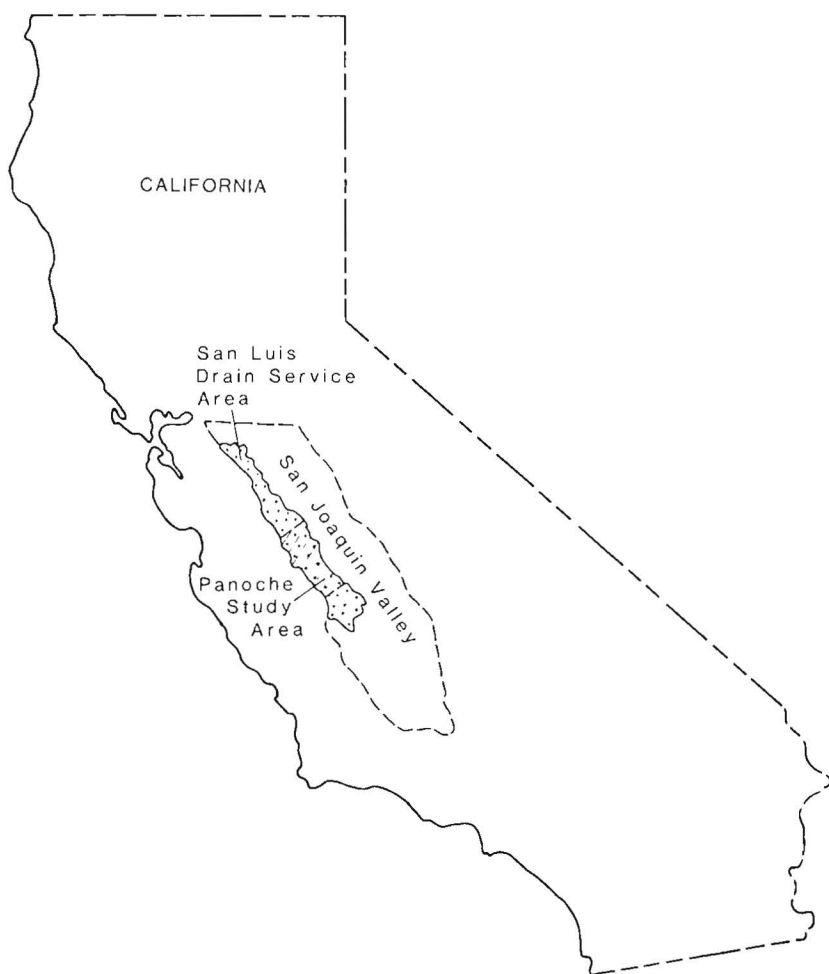


Fig. 9-1. Index map showing the location of the San Luis Drain Service Area and the Panoche Study Area in the San Joaquin Valley, California.

ment were found in birds, fish, and plants exposed to the water. The concentrations of Se found in water in field-drain sumps ranged from 84 to 4200  $\mu\text{g/L}$ ; the concentration in San Luis Drain water averaged about 300  $\mu\text{g/L}$  (Presser & Barnes, 1985).

Field-sump water in the irrigation district near the lower end of the Panoche and Cantua Creek alluvial fans contained higher concentrations of Se than other localities in the district (Deverel et al., 1984). Based on this evidence from water, we investigated the distribution of numerous elements in the soils on these same two alluvial fans. The purpose of this study was to determine the optimum number of element associations that would describe the distribution of elements in the soils and to determine what natural fea-

tures might control those associations. A second objective was to identify sources and sinks for environmentally important trace elements.

Sediments in the San Joaquin Valley are derived from both the Diablo Range on the west and the Sierra Nevada Range on the east, but the majority probably come from granite and metamorphosed sedimentary and igneous rocks on the east side of the valley (Harradine, 1950). The west side of the valley features coalescing alluvial fans that originate at the base of the Diablo Range and slope toward the northeast. The maximum depth of valley fill under these fans exceeds 300 m (1000 feet) (Lettis, 1982). The two major fans, from Panoche Creek and Cantua Creek, are fed from extensive drainage basins in the Diablo Range. Several smaller fans are fed by local, intermittent streams in the foothills near Monocline Ridge and Panoche Hills, to the north of Panoche Creek. Monocline Ridge is underlain in part by marine shales that are prone to slumping and sliding. These products of mass wasting are transported onto the alluvial fans during floods as clay-rich mudflows. The resulting fan deposits are subject to subsidence (Bull, 1964).

## MATERIALS AND METHODS

Samples of soil were collected from alluvial soil profiles at 721 sites located on a 1.6-km (1-mile) square grid (Fig. 9-2). Each sample was obtained with a 7.6-cm (3-inch) diameter stainless-steel barrel auger from the depth interval of 168 to 183 cm (66-72 inch). The interval is not only one of convenience, but the sample is believed to be representative, because Severson et al. (1986) reported that Se concentration does not vary with depth. Some samples near the lower extremities of the alluvial fans were collected within the saturated zone.

Samples were air-dried, and the aggregates were crushed and sieved through a 2-mm stainless steel screen. A subsample was ground in a ceramic mill to pass a 100-mesh screen and analyzed for total concentrations of 43 elements (Table 9-1). The following eight elements were below detection limits for all samples, shown as mg/kg: bismuth (Bi)—10, europium (Eu)—2, gold (Au)—8, holmium (Ho)—4, silver (Ag)—2, tantalum (Ta)—40, Tin (Sn)—20, and uranium (U)—100.

Most elements were detected by inductively coupled argon plasma-atomic emission spectrometry (ICP) after digesting the samples in acids (HF, HCl, HNO<sub>3</sub>, HClO<sub>4</sub>) and bringing to a constant volume in 0.2 M HNO<sub>3</sub> (Crock et al., 1983). Analyses for As and Se were by hydride generation-atomic absorption spectrometry after digestion in acids (HF, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) and volume adjustment in 2 M HCl (Briggs & Crock, 1986; Crock & Lichte, 1982). Mercury was determined by cold vapor atomic absorption after digestion in a Na<sub>2</sub>CrO<sub>4</sub>/HNO<sub>3</sub> solution (Koirtyohann & Khalli, 1976; Kennedy & Crock, 1987). Analyses for total C were done in a Leco automated carbon analyzer and for total S in a Leco automated sulfur analyzer (LECO Corp., St. Joseph, MI).

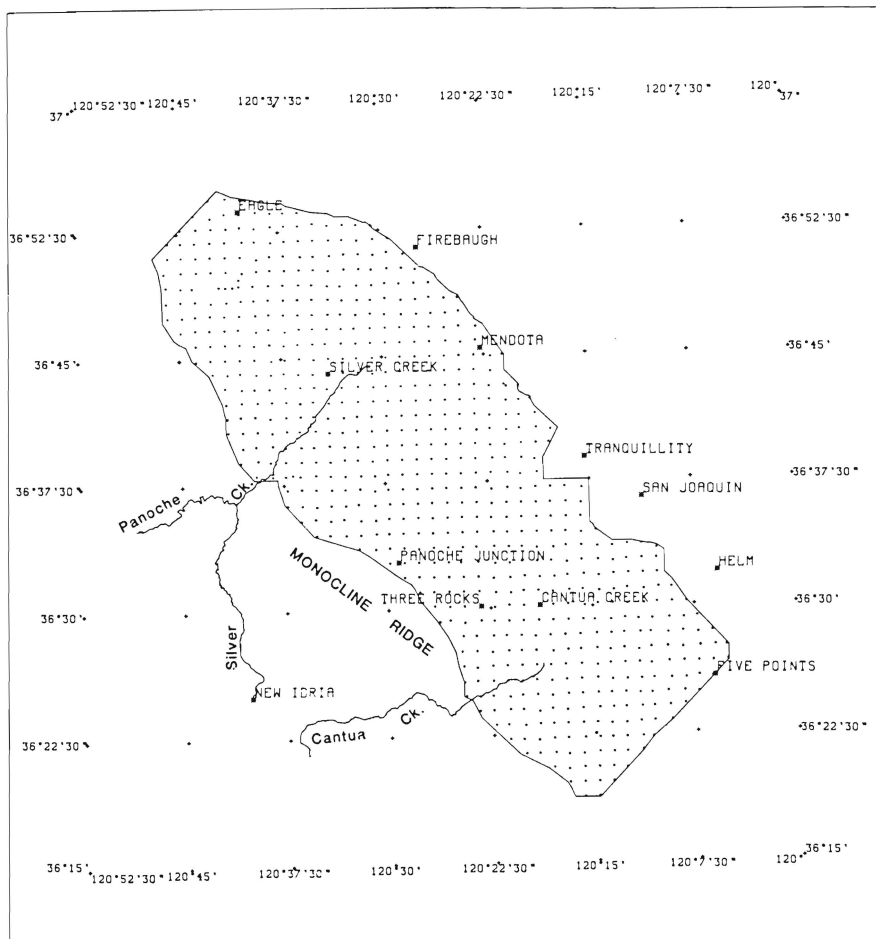


Fig. 9-2. Map of 721 soil sampling sites in the Panoche Study Area, western Fresno County, California.

The normal range of concentrations for most elements is within the range of detection by the analytical methods, but for some elements numerous samples were reported as below the limit of detection (censored). Censored data were arbitrarily replaced by a value 0.7 times the lower limit of detection for elements where censored data did not exceed 20% of the samples so that a complete data set was available for statistical computations. Interpretations were not significantly affected by this number of replacements. If elements had  $> 50\%$  of the total variance, the element was omitted from further consideration. Of the original 43 elements, 26 (indicated by the asterisks in Table 9-1) were used in the factor analysis.

### Factor Analysis

Factor analysis is a multivariate procedure that provides for classifying either by groups of samples (Q-mode) each with similar compositions or by



Table 9-1. Elements measured in soils, methods of determination, lower limits of detection, detection ratio, and percent error variance.

Element†	Method‡	Lower limit of detection§	Detection ratio¶	Error variance, % #
*Al	ICP	0.05%	721:721	12
As	HG	0.1	721:721	54
Ba	ICP	1	721:721	54
Be	ICP	1	669:721	0
*C	LA	0.1%	719:721	3
*Ca	ICP	0.05%	721:721	2
Cd	ICP	2	2:721	--
*Ce	ICP	4	721:721	16
*Co	ICP	1	721:721	7
*Cr	ICP	1	721:721	11
*Cu	ICP	1	721:721	6
*Fe	ICP	0.05%	721:721	4
*Ga	ICP	4	721:721	18
*Hg	CV	0.02	579:721	17
*K	ICP	0.05%	721:721	4
La	ICP	2	721:721	24
*Li	ICP	2	721:721	5
*Mg	ICP	0.005%	721:721	3
*Mn	ICP	4	721:721	4
Mo	ICP	2	89:721	--
*Na	ICP	0.005%	721:721	9
Nd	ICP	4	721:721	38
*Ni	ICP	2	721:721	2
*P	ICP	0.005%	721:721	9
Pb	ICP	4	721:721	60
*S	LA	0.01%	679:721	3
*Sc	ICP	2	721:721	7
*Se	HG	0.1	713:721	21
*Sr	ICP	2	721:721	6
*Th	ICP	4	716:721	24
*Ti	ICP	0.005%	721:721	13
*V	ICP	1	721:721	7
*Y	ICP	2	721:721	11
Yb	ICP	1	713:721	55
*Zn	ICP	4	721:721	8

† \* Refers to elements included in factor analysis.

‡ ICP, inductively coupled argon plasma-atomic emission spectrometry. HG, hydride generation-atomic absorption spectrometry. LA, Leco analyzer. CV, cold vapor atomic absorption.

§ Values in mg/kg (ppm) except as noted percent. Detection limits in mg/kg for eight elements never detected in any samples were: Ag(2), Au(8), Bi(10), Eu(2), Ho(4), Sn(20), Ta(40), and U(100).

¶ Number of values reported above lower limit of detection/total number samples analyzed.

# Laboratory-error variance as percentage of total variance; --, not computed.

groups of elements (R-mode) that commonly associate with each other (Joreskog et al., 1976). The R-mode, which is based on simple correlations between the elements, was used in this study because element associations have previously been useful in illustrating element distributions and defining source materials (Tidball, 1984). The data were transformed to logarithms before the analysis because the frequency distributions are more nearly normal on a log scale, and correlation coefficients are sensitive to normality.

In R-mode, elements may be represented as vectors projected into  $n$ -dimensional space, where  $n$  equals the number of elements, and the coordinate axes are usually orthogonal. Consider the simple case where  $n$  equals two,  $x$  and  $y$ . The location of a vector in that space is specified by the coordinates or projections of the end of the vector onto each axis, respectively. If the vector, for example, is close to the  $x$  axis, it has a large  $x$  coordinate and a small  $y$  coordinate. In factor terminology the axis is called a *factor*, and it represents a theoretical assemblage of elements or an end-member composition. The  $x$ - and  $y$ -coordinate values are called *factor loadings*. Because the element vector in this sample is close to the  $x$  factor, that element is closely related to the theoretical  $x$  composition and unrelated to the  $y$  composition.

The maximum number of dimensions available in the factor space is equal to the number of elements in the data set (26 in this study). Thus, the location of any vector in that space can be precisely described in 26 dimensions, and the composition of each factor consists of one element. Because two or more elements may be strongly correlated with each other, there is redundancy in the data, and those elements can be combined into a single factor. This reduces the number of dimensions needed in the factor space to describe the location of the vector. The objective of factor analysis, therefore, is to derive the simplest model (minimum number of factors) that will still yield a reasonable explanation of the data.

In addition to a matrix,  $a$ , of factor loadings, another matrix of values,  $A$ , called *factor scores*, is computed such that the product of the two matrices approximately reproduces the original data matrix,  $X$ , as follows:

$$aA = X + R \quad [1]$$

where  $R$  is a residual that approaches zero as the factor model describes ever-more of the variance in the data.

Just as a sample is characterized by a number of single-variate attributes (Ca, Mg, and so forth), it also is characterized by a set (one score for each factor) of multivariate attributes (factor scores). The scores for any one factor are dimensionless numbers with a near-normal frequency distribution, a mean of zero, and a standard deviation of one. Values in the positive tail of the distribution represent a sample composition that is very similar to the factor composition. Values near zero represent a sample composition that has no similarity to the factor. Values in the negative tail of the distribution represent a sample composition that is also dissimilar to the factor composition but in a consistent manner—if certain dominant elements that characterize the factor are present, then certain other elements will be absent and vice versa.

Previously, it was stated that factors are usually orthogonal, but this is not a requirement. Orthogonal factors are uncorrelated. This is useful in some studies, but the disadvantage is that the theoretical factor compositions can be unrealistic by containing negative amounts of some constituents, a circumstance that is difficult to explain. An alternative applied in this study was to rotate the factors from an orthogonal position to an oblique posi-

tion. This means the angle between the factors was changed from a right angle to an acute angle by rotating the factors to positions where each coincides with an outlying element vector, respectively. Though the factor compositions are now partially correlated, they are more realistic.

Certain elements dominate the composition of each factor. The relative importance of an element in a factor composition is quantified by the correlation coefficient computed between a factor score and the concentrations of each element, respectively. The largest coefficient indicates the most dominant element. A coefficient can be either positive or negative, indicating that an element is commonly either enriched in the composition or depleted, respectively. In describing the composition of each factor, only the more dominant elements are cited, but in fact the composition includes all 26 elements, though some have a very small presence.

### Selecting an Optimum Factor Model

Finding an optimum factor model requires judgment in which the objective of simplifying the model as much as possible is balanced against the necessity to maximize the explanation of the variance in the data. The process is in part one of trial and error looking at different models. As the number of factors is increased, some associations of dominant elements persist while others tend to partition into smaller groups. Factors 1 and 2 are examples of stable associations of elements. They are stable because the controlling processes are dominant, and the variance of the elements involved is small so a very simple factor model (few factors) readily identifies the associations. With the addition of each successive factor, an additional dimension is added to the factor space, and additional elements with larger variance begin to be explained. Finally, a unique factor that contains only one dominant element is isolated. Such a factor typically appears only after there are already several factors in the model, and a major part of the variance has been explained. It is advisable to reject single-element factors, because the model has become unnecessarily complex and has not effectively explained the variance because of subtle, unknown process-controlled reasons, or more commonly, because of excessive analytical error. The final measure, however, is that the model must be explainable and provide insight to the conditions or processes that control the composition of the soils in the study area.

## RESULTS AND DISCUSSION

The optimum model derived from factor analysis has five factors. Although the composition of each factor consists of all 26 elements, different elements dominate the compositions of each factor. Those dominant elements (correlation coefficients  $>0.4$ ) for each factor are shown in Table 9-2.

The scores for each factor are plotted in Fig. 9-3 to 9-7 as a continuous surface of values. The original grid of scores measured at 1.6-km (1-mile) intervals was interpolated to a finer and smoother surface with a grid inter-

Table 9-2. Factor compositions. Elements are arranged in descending order of correlation coefficient, which indicates relative importance of the element.

Factors									
1		2		3		4		5	
Al	0.95	Ni	0.95	Se	0.84	Ca	0.90	C	0.87
Ti	0.94	Mg	0.92	S	0.50	Sr	0.78	Hg	0.51
Ga	0.94	Cr	0.91			C	0.42		
Y	0.91	Co	0.89			S	0.40		
Ce	0.90	Mn	0.64						
Sc	0.89	Fe	0.64						
Fe	0.88	Cu	0.61						
Li	0.88								
Zn	0.84								
V	0.84								
Cu	0.83								
Th	0.72								
Mn	0.65			Na	-0.79				

val of 0.5 km using universal kriging (Tidball et al., 1986). Kriging is a method of estimating values at intermediate points between measured points that accounts for the weighting effect of all neighboring values, including their variance, within a zone of influence. The gridded surface of scores is shown on maps as shades of gray each assigned to selected percentiles of the frequency distribution of gridded values.

Factor 1 includes Al, Ti, Ga, Y, Ce, and others, all elements that suggest felsic source materials. The largest scores occur south of Mendota within the valley trough (Fig. 9-3). Soil samples from this area contain micaceous sediments. These and other soils near the central part of the valley (east margin of the study area) probably reflect sediments from granitic rocks in the Sierra Nevada. The explanation for other soils with large scores near Eagle is more uncertain. It is unknown whether the felsic influence comes from the coast ranges or is a residual effect of sediments being swept across the valley from the east side during floods.

Factor 2 is comprised of dominant elements, Ni, Mg, Cr, and Co, which are elements derived from serpentine. The scores outline the alluvial fan of Cantua Creek and to a lesser extent the alluvial fan of Panoche Creek (Fig. 9-4). A large intrusive body of serpentine is located just south of New Idria. Cantua Creek conveys sediment from this source directly to the valley. Serpentine gravels are abundant near the head of the fan, but the largest scores occur closer to the valley trough where the soils are finer-textured. Serpentine sediments also enter the study area from the south. Los Gatos Creek, which enters the valley just south of the study area, drains the southern exposure of the serpentine body.

Factor 3 is a Se-S factor. Sodium is negatively associated with this factor, which indicates that where Se occurs Na does not and vice versa. Common occurrences of Se with S probably reflect the similar chemical behavior of these two elements, but a chemical bond between them is not necessarily implied. Factor 3 scores are highest along the valley edge near Panoche Junc-

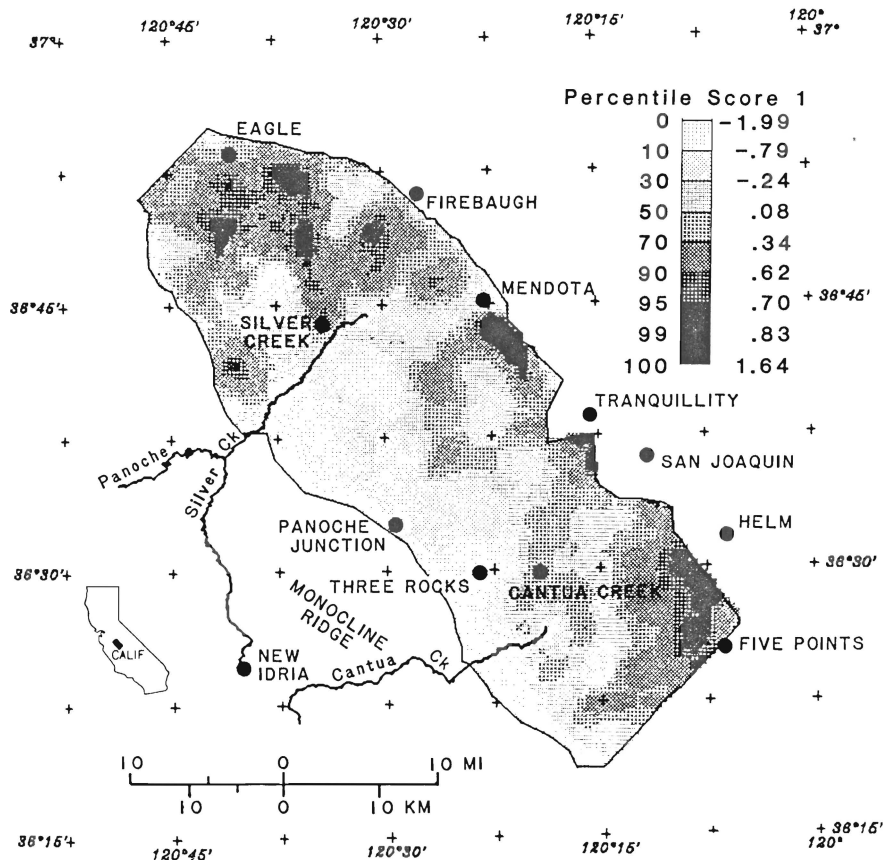


Fig. 9-3. Map of Factor 1 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

tion and just north of Panoche Creek (Fig. 9-5). Sediments of this type apparently are not derived from either the Panoche or Cantua Creek watersheds. The locale of the high scores near Panoche Junction is characterized by mud-flow deposits that spread into the valley from adjacent, fine-grained, sedimentary rocks of both marine and nonmarine origin located near Monocline Ridge. Selenium and S are dispersed out from the high score area with some movement downslope toward areas where the water table is close to the surface. Because the shallow groundwater at the lower end of the fan near Mendota and Firebaugh contains elevated concentrations of Se (up to 4000  $\mu\text{g/L}$ ) (Deverel et al., 1984), some unknown fraction of the total Se has probably been transported by water.

Factor 4 is interpreted as an alkaline-earth factor with the dominant elements Ca and Sr and less dominant elements C and S. The latter elements probably occur as the anions, carbonate, and sulfate. The soils are commonly effervescent in HCl, and gypsum is abundant. The distribution of Factor

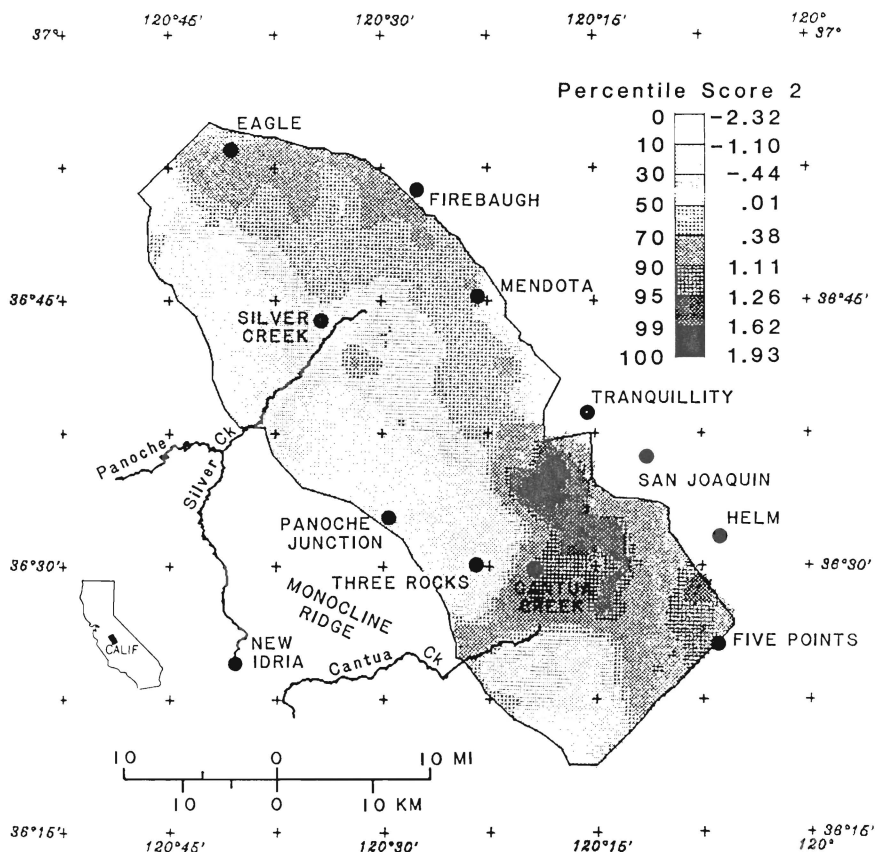


Fig. 9-4. Map of Factor 2 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

4 scores (Fig. 9-6) suggests that one area of high scores is at the western edge of the valley near Monocline Ridge, the locale of mudflow deposits where Se was implicated. Another area of high scores is in the valley trough at the eastern edge of the study area. Gypsum and carbonate are not only common in the soils of these areas, but they are also abundant in sedimentary rocks in the Monocline Ridge area. Thus, the origin of gypsum and carbonate in the soils near the valley edge could be either detrital or pedogenic or both. A dispersion train extends downslope, suggesting transport either by erosion or by dissolution and reprecipitation. The valley trough area is adjacent to Fresno Slough, an old channel for water overflow from the Tulare Lake basin to the south. The soils developed on clay-rich sediments where evaporites from a high water table accumulated. The distribution pattern indicates that the probable origin of the evaporites is elsewhere in the upper part of the San Joaquin Valley, but a contribution from the Monocline Ridge source is also possible.

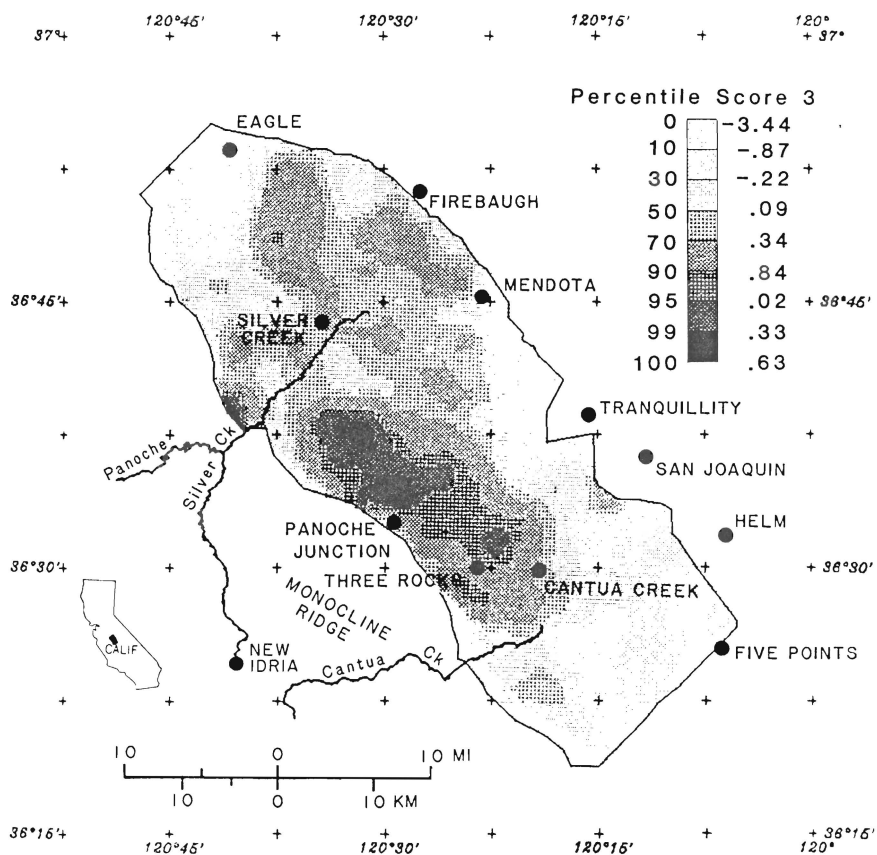


Fig. 9-5. Map of Factor 3 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

Carbon is the dominant element of Factor 5, and Hg is the less dominant companion. The pattern of higher scores outlines the alluvial fan of Panoche Creek and to a lesser extent that of Cantua Creek (Fig. 9-7). Factor analysis has partitioned C between Factors 4 and 5, indicating two different associations and distributions. The high scores of Factor 4 are located between the major alluvial fans, and those of Factor 5 are located on those fans. The mode of occurrence in Factor 4 is probably inorganic, whereas Factor 5 is interpreted as organic. The reasoning is that the greater supply of water on the fans stimulated the accumulation of organic C from greater vegetative production. Some C could also be deposited from flood water.

Mercury originates from the vicinity of the New Idria Hg deposit near the head of Silver Creek. Both Silver Creek and Cantua Creek discharge Hg to the valley, but the discharge of sediments from the 100-yr-old mining operation (idle since 1972) at New Idria directly into Silver Creek probably accounts for the greater deposition on the Panoche Creek fan. The common

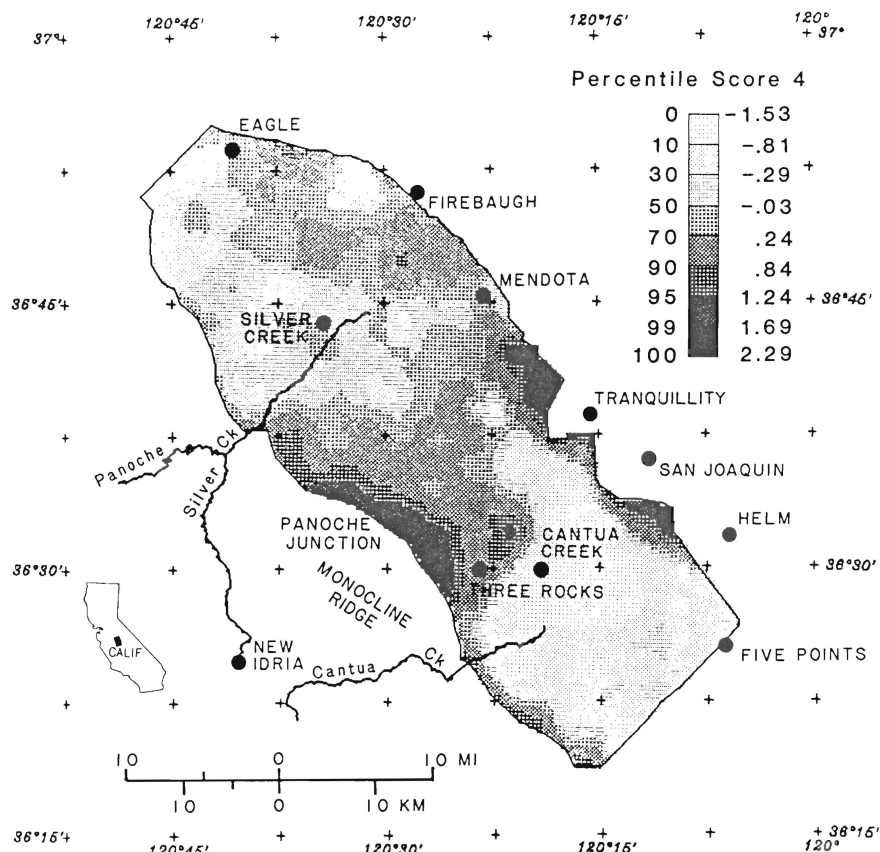


Fig. 9-6. Map of Factor 4 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

occurrence of C and Hg in the same location suggests a common controlling process. Perhaps the Hg forms complexes with organic material in the soils (Adriano, 1986).

Factors 3 and 4 when considered together exhibit two features: (i) at the west side of the study area near Panoche Junction Ca, Sr, C, S, and Se are abundant, and Na is impoverished, and (ii) at the east side of the study area Ca, Sr, C, and S are also abundant, Na is moderately high, but Se is absent. The inverse relation between Se and Na indicates the two elements do not share the same spatial distribution. Sulfur may be viewed as being partitioned between these two associations occurring in higher concentration with the Na on the east side than with the Se on the west side. If Se and S have a similar chemical behavior, then why doesn't Se also exhibit higher concentrations on the east side? Lakin and Davidson (1973) state that

In weathering, selenium and sulfur tend to be separated, in large part because selenium becomes fixed in insoluble basic ferric selenites. Only in an alkaline oxidizing environment is selenium oxidized to the soluble



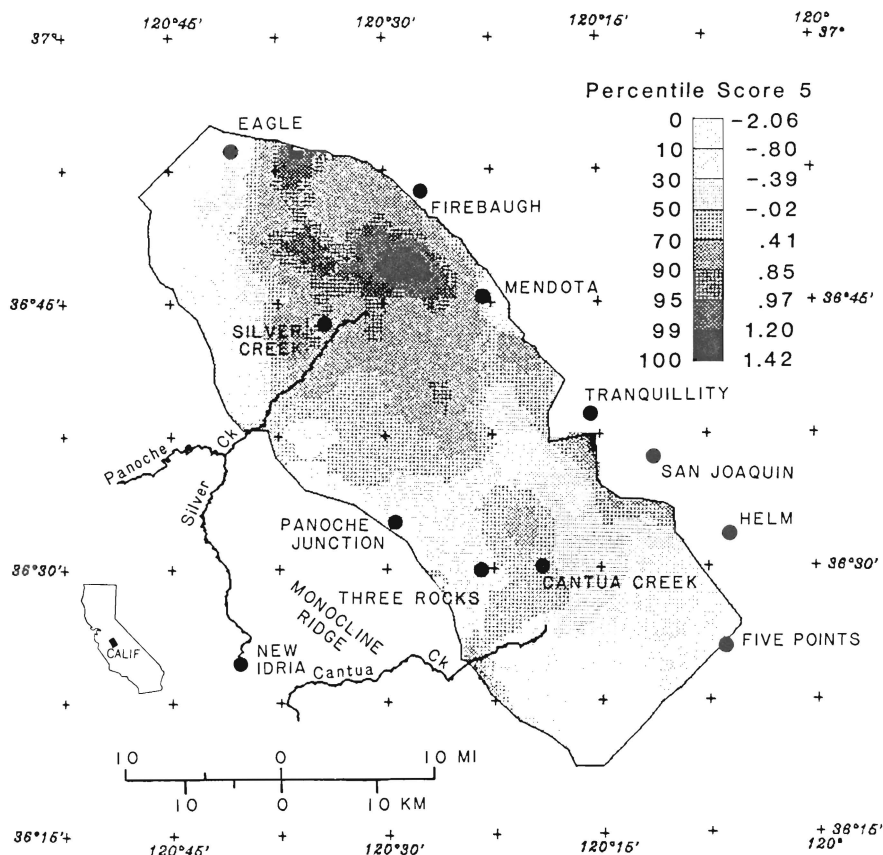


Fig. 9-7. Map of Factor 5 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

selenate form; sulfur, however, is even more readily oxidized to highly soluble sulfate and is carried away in surface and ground waters. As a result, selenium is present neither in sulfate deposits nor in sedimentary sulfur deposits.

This might explain the absence of Se in the east side evaporites. It is unknown whether Se and S occur in the same minerals on the west side, but if different solubilities prevail the two elements may occur in independent forms.

Factor analysis has been an effective tool to identify five fundamental element associations or compositions. The make up of each association and its distribution were interpreted to define either source materials, or transport or pedogenic processes. Although a few soils with large scores on each factor are type examples of each composition, respectively, many other soils are mixtures of the type compositions. The soils were developed in areas where sediments from different sources or different processes overlap. The study has shown that several environmentally important elements occur in the irrigation district that could enter the drainage system.

Selenium is added to the valley sediments in moderate amounts all along the west side of the San Joaquin Valley (R.R. Tidball, 1985, unpublished data), probably as detritus from shales. In the fan areas, Se may be diluted by barren sediments as well as be more readily dissolved and removed in a well watered system. In the interfan areas, the solution of Se would be diminished by the lack of a solvent, ineffective removal, and possible excess evaporation. Superimposed on this scenario is an anomalous occurrence of Se near Monocline Ridge. Selenium is hosted in sedimentary rocks, particularly marine shales, that border the valley (R.R. Tidball, 1988, unpublished data). The ultimate source of that Se is yet another question. Perhaps Se in a broad halo around the Hg deposit at New Idria migrated into the adjacent sedimentary materials.

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